

## **General Disclaimer**

### **One or more of the Following Statements may affect this Document**

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.



Interactions between Oxygen and Nitrogen: O—N, O—N<sub>2</sub>, and O<sub>2</sub>—N<sub>2</sub>

JOSEPH T. VANDERSLICE, EDWARD A. MASON, AND WILLIAM G. MAISCH

NASA FILE COPY

Loan expires on last  
date stamped on back cover.

PLEASE RETURN TO

REPORT DISTRIBUTION SECTION  
LANGLEY RESEARCH CENTER  
NATIONAL AERONAUTICS AND  
SPACE ADMINISTRATION

Langley Field, Virginia

Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 31, No. 3, pp. 738-746, September, 1959

NOV 24 1959

## Interactions between Oxygen and Nitrogen: O—N, O—N<sub>2</sub>, and O<sub>2</sub>—N<sub>2</sub>†

JOSEPH T. VANDERSLICE, EDWARD A. MASON, AND WILLIAM G. MAISCH

*Institute for Molecular Physics, University of Maryland, College Park, Maryland*

(Received March 23, 1959)

Potential energy curves for O—N interactions corresponding to the  $X^2\Pi_{1/2}$ ,  $X^2\Pi_{3/2}$ ,  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  states of nitric oxide have been calculated from spectroscopic data by the Rydberg-Klein-Rees method. Curves for the  $4\Pi$ ,  $2\Sigma$ ,  $4\Sigma$ ,  $6\Sigma$ , and  $6\Pi$  states have been obtained from limited spectroscopic results and from relations derived from approximate quantum-mechanical calculations. Two semi-independent calculations have been made, and are in good agreement with each other. The quantum-mechanical relations also lead to approximate curves for the O—N<sub>2</sub> and O<sub>2</sub>—N<sub>2</sub> interactions over a limited range. The O<sub>2</sub>—N<sub>2</sub> interaction is consistent with one valid at larger separation distances which has been derived from high-temperature gas viscosity data.

### INTRODUCTION

INTERACTIONS among oxygen and nitrogen atoms and molecules are of interest in a number of connections, such as the calculation of the transport properties of air at very high temperatures,<sup>1</sup> and various upper atmospheric phenomena. Potential energy curves for interactions between ground-state nitrogen atoms and molecules have already been reported.<sup>2</sup> The present paper deals with the interactions between an oxygen atom and a nitrogen atom, and with the O—N<sub>2</sub> and O<sub>2</sub>—N<sub>2</sub> interactions. Certain other interactions which could also be handled by the present procedures, such as N—O<sub>2</sub> and N—NO, have been omitted because of their relative rarity and their probable unimportance for most phenomena of interest.

The most important interactions, at least as far as calculation of transport properties is concerned, are those between the ground state atoms and molecules. When a ground-state oxygen atom ( $^3P$ ) and a ground-state nitrogen atom ( $^4S$ ) approach each other, six different interactions are possible,<sup>3</sup> corresponding to the spectroscopic states  $2\Sigma$ ,  $2\Pi$ ,  $4\Sigma$ ,  $4\Pi$ ,  $6\Sigma$ , and  $6\Pi$  of the NO molecule. Considerable spectroscopic data are available for the ground state ( $X^2\Pi$ ), and a limited amount seems to be available for the  $4\Pi$  state, which is probably a bound state.<sup>4,5</sup> The other four states are probably all repulsive,<sup>4</sup> or at best very weakly bound, and there is practically no experimental information on any of them. An accurate potential energy curve for the  $X^2\Pi$  ground state can be calculated from the spectroscopic data by the Rydberg-Klein-Rees (RKR)

method.<sup>2,6</sup> A Hulburt-Hirschfelder curve<sup>7</sup> for the  $4\Pi$  state can be based on the limited amount of spectroscopic data available and on the close analogy of NO with the isoelectronic molecule O<sub>2</sub><sup>+</sup>.

Rather simple quantum-mechanical considerations can be used to establish relationships among the six different states of NO. From these relationships the long-range "tails" of the  $2\Sigma$ ,  $4\Sigma$ ,  $6\Sigma$ , and  $6\Pi$  curves can be calculated once the  $2\Pi$  and  $4\Pi$  curves are known. A semi-independent calculation of the long-range "tails" of the  $4\Pi$ ,  $2\Sigma$ ,  $4\Sigma$ ,  $6\Sigma$ , and  $6\Pi$  curves can also be made, based on the  $2\Pi$  curve and the  $X^1\Sigma_g^+$  curve of N<sub>2</sub>. Agreement between the two calculations is excellent. The usual quantum-mechanical approximation of perfect pairing, which worked well in the case of nitrogen,<sup>2</sup> cannot be applied directly to NO, since NO has an odd electron which is necessarily unpaired. In somewhat different language, NO may be said to have a "three-electron bond," for which the perfect pairing approximation as such is inadequate. However, an adequate description in terms of a combination of molecular orbitals and the perfect pairing approximation can be given along the lines suggested by Linnett.<sup>8</sup> This description also leads to simple relationships involving molecules, so that the O—N<sub>2</sub> and O<sub>2</sub>—N<sub>2</sub> interactions can be derived from the results on the N—O interactions. The O<sub>2</sub>—N<sub>2</sub> interaction so obtained is consistent, after averaging over all orientations, with one valid at larger separation distances which is derived from high temperature gas viscosity data.

Results for the  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  are also included. These are all bound states and were calculated by the RKR method from available spectroscopic data. They are all related to dissociation products involving excited atoms.

† This research was supported in part by the National Aeronautics and Space Administration.

<sup>1</sup> C. F. Hansen, NACA Tech. Note 4150 (1958); see this report for references to earlier work.

<sup>2</sup> Vanderslice, Mason, and Lippincott, J. Chem. Phys. **30**, 129 (1959).

<sup>3</sup> G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1953), pp. 318-319.

<sup>4</sup> R. S. Mulliken, Revs. Modern Phys. **4**, 1 (1932).

<sup>5</sup> R. S. Mulliken, *The Threshold of Space* (Pergamon Press, Ltd., New York, 1957), p. 123.

<sup>6</sup> (a) R. Rydberg, Z. Physik **73**, 376 (1931); (b) O. Klein, Z. Physik **76**, 226 (1932); (c) A. L. G. Rees, Proc. Phys. Soc. (London) **A59**, 998 (1947); (d) Vanderslice, Mason, Maisch, and Lippincott, J. Mol. Spectroscopy **3**, 17 (1959).

<sup>7</sup> H. M. Hulburt and J. O. Hirschfelder, J. Chem. Phys. **9**, 61 (1941).

<sup>8</sup> J. W. Linnett, J. Chem. Soc. **1956**, 275.

## BOUND STATES OF NO

The potential energy curves for the bound states  $X^2\Pi$ ,  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  were obtained by the RKR method.<sup>2,6</sup> The RKR calculation is a semiclassical one which utilizes spectroscopic data to determine the values of the intermolecular distance corresponding to the classical turning points in the vibrational motion of the molecule. Quantization of the vibrational action integral and the angular momentum phase integral leads to the following expressions for the turning points,  $r_{\max}$  and  $r_{\min}$ , in terms of spectroscopic data:

$$r_{\max} = [(f/g) + f^2]^{\frac{1}{2}} + f, \quad (1)$$

$$r_{\min} = [(f/g) + f^2]^{\frac{1}{2}} - f, \quad (2)$$

where  $f$  and  $g$  are functions of the vibration-rotation energy levels. The expressions for  $f$  and  $g$  are particularly simple<sup>6c</sup> if the vibration-rotation energy  $E(v, J)$  can be expressed as a quadratic in  $v$ :

$$E(v, J) = \omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2})^2 - \alpha(v + \frac{1}{2})J(J+1) + BJ(J+1) + DJ^2(J+1)^2 + \dots, \quad (3)$$

where  $v$  and  $J$  are the usual vibration-rotation quantum numbers, and  $\omega$ ,  $\omega x$ ,  $\alpha$ ,  $B$ ,  $D$ , etc., are constants. In this case the expression for  $f$  and  $g$  for the rotationless ( $J=0$ ) state are

$$f = \left( \frac{h}{8\pi^2\mu c \omega x} \right)^{\frac{1}{2}} \ln \left[ \frac{(\omega^2 - 4\omega x V)^{\frac{1}{2}}}{\omega - (4\omega x V)^{\frac{1}{2}}} \right], \quad (4)$$

$$g = \left[ \frac{2\pi^2\mu c}{h(\omega x)^3} \right]^{\frac{1}{2}} \left\{ \frac{1}{4}\alpha(\omega x V)^{\frac{1}{2}} + (2B\omega x - \alpha\omega) \times \ln \left[ \frac{(\omega^2 - 4\omega x V)^{\frac{1}{2}}}{\omega - (4\omega x V)^{\frac{1}{2}}} \right] \right\}, \quad (5)$$

where  $\mu$  is the reduced mass,  $h$  is Planck's constant,  $c$  is the velocity of light,  $V$  is the energy (in  $\text{cm}^{-1}$ ) above the bottom of the potential curve,  $f$  is in cm, and  $g$ ,  $\omega$ ,  $\omega x$ , and  $B$  are all in  $\text{cm}^{-1}$ . If  $E(v, J)$  cannot be represented over the entire experimental range by a quadratic, it can usually be expressed as different quadratics over different ranges, so that the entire experimental region can be covered by a series of quadratics. In such cases the expressions for  $f$  and  $g$  are a little more complicated,<sup>2,6c,6d</sup> but the potential energy curves can still be calculated rapidly and accurately.

The results obtained from the application of the RKR method to the  $X^2\Pi_1$ ,  $X^2\Pi_2$ ,  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  states are given in Tables I-VIII. The experimental data were obtained from the following sources: Gillette and Eyster<sup>9</sup>; Jenkins, Barton, and Mulliken<sup>10</sup>; Brook and Kaplan<sup>11</sup>; Lagerqvist and

TABLE I. Potential energy of the  $X^2\Pi_1$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$r_{\max}(\text{\AA})$	$r_{\min}(\text{\AA})$	$V(\text{ev})$
0	948.5	1.210	1.113	0.1176
1	2 825	1.253	1.082	0.3503
2	4 673	1.284	1.063	0.5795
3	6 493	1.312	1.049	0.8051
4	8 285	1.337	1.036	1.027
5	10 048	1.360	1.026	1.246
6	11 784	1.383	1.017	1.461
7	13 492	1.404	1.008	1.673
8	15 172	1.425	1.001	1.881
9	16 824	1.445	0.994	2.086
10	18 448	1.465	0.987	2.288
11	20 044	1.486	0.982	2.485
12	21 613	1.505	0.976	2.680
13	23 152	1.525	0.971	2.871
14	24 665	1.545	0.966	3.058
15	26 149	1.564	0.962	3.242
16	27 605	1.584	0.957	3.423
17	29 034	1.604	0.953	3.600
18	30 434	1.623	0.949	3.774
19	31 805	1.643	0.945	3.944
20	33 141	1.663	0.940	4.109
21	34 443	1.684	0.937	4.271
22	35 714	1.704	0.933	4.428
23	36 953	1.725	0.929	4.582

<sup>a</sup> Experimental data from references 9-11.

Miescher<sup>12</sup>; Barrow and Miescher<sup>13</sup>; Herzberg, Lagerqvist, and Miescher<sup>14</sup>; Sutcliffe and Walsh<sup>15</sup>; Feast<sup>16</sup>; Tanaka, Seya, and Mori<sup>17</sup>; and Miescher.<sup>18</sup>

An additional complication in NO is the coupling of the rotation and electronic motion, and its effect on the RKR calculations requires further explanation. The resultant splitting is very small and may be neglected for all states except the ground  $X^2\Pi$  state, for which the splitting is equal to  $121 \text{ cm}^{-1}$ , or about 0.2% of the dissociation energy. The coupling scheme for the  $X^2\Pi$  state is intermediate between Hund's cases (a) and (b), and the expression for the rotational energy is more complicated than Eq. (3).<sup>19</sup> In this case, since the spin uncoupling is small, the energy can be written in the form<sup>19</sup>

$$E(v, J) = \omega(v + \frac{1}{2}) - \omega x(v + \frac{1}{2})^2 + B_{\text{eff}}J(J+1) + DJ^2(J+1)^2 + \dots, \quad (6)$$

where

$$B_{\text{eff}} = B_v \left( 1 \pm \frac{B_v}{A\Lambda} + \dots \right), \quad (7)$$

$$B_v = B - \alpha(v + \frac{1}{2}) + \dots, \quad (8)$$

<sup>12</sup> A. Lagerqvist and E. Miescher, *Helv. Phys. Acta* **31**, 221 (1958).

<sup>13</sup> R. F. Barrow and E. Miescher, *Proc. Phys. Soc. (London)* **A70**, 219 (1957).

<sup>14</sup> Herzberg, Lagerqvist, and Miescher, *Can. J. Phys.* **34**, 622 (1956).

<sup>15</sup> L. H. Sutcliffe and A. D. Walsh, *Proc. Phys. Soc. (London)* **A66**, 209 (1953).

<sup>16</sup> M. W. Feast, *Can. J. Research* **28A**, 488 (1950).

<sup>17</sup> Tanaka, Seya, and Mori, *J. Chem. Phys.* **19**, 979 (1951).

<sup>18</sup> E. Miescher, *Helv. Phys. Acta* **29**, 401 (1956).

<sup>19</sup> Reference 3, p. 218 ff.

<sup>9</sup> R. H. Gillette and E. H. Eyster, *Phys. Rev.* **56**, 1113 (1939).

<sup>10</sup> Jenkins, Barton, and Mulliken, *Phys. Rev.* **30**, 150 (1927).

<sup>11</sup> M. Brook and J. Kaplan, *Phys. Rev.* **96**, 1540 (1954).

TABLE II. Potential energy of the  $X^2\Pi_{1/2}$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V^b$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	948.5	1 074	1.196	1.099	0.1176
1	2 825	2 951	1.239	1.068	0.3503
2	4 673	4 799	1.270	1.049	0.5795
3	6 493	6 619	1.297	1.034	0.8051
4	8 285	8 411	1.323	1.022	1.027
5	10 048	10 172	1.346	1.012	1.246
6	11 784	11 910	1.368	1.002	1.461
7	13 492	13 618	1.390	0.994	1.673
8	15 172	15 298	1.410	0.986	1.881
9	16 824	16 950	1.431	0.979	2.086
10	18 448	18 574	1.451	0.973	2.288
11	20 044	20 170	1.471	0.967	2.485
12	21 613	21 739	1.491	0.962	2.680
13	23 152	23 278	1.510	0.956	2.871
14	24 663	24 789	1.530	0.951	3.058
15	26 145	26 271	1.550	0.947	3.242
16	27 599	27 725	1.569	0.942	3.422
17	29 024	29 150	1.589	0.938	3.599
18	30 423	30 549	1.609	0.934	3.772
19	31 790	31 916	1.629	0.930	3.942
20	33 124	33 250	1.649	0.926	4.107
21	34 424	34 550	1.669	0.922	4.269
22	35 695	35 821	1.690	0.918	4.426
23	36 938	37 064	1.710	0.915	4.580

<sup>a</sup> Experimental data from references 9-11.<sup>b</sup>  $T_e$  is the energy difference between the bottom of the potential curve for the state in question and the bottom of the curve for the  $X^2\Pi_{1/2}$  state.

in which  $A$  is the coupling constant and  $\Lambda$  is the component of the electronic orbital angular momentum along the internuclear axis. Terms independent of  $v$  and  $J$  have been omitted. Hence the energy expression is still of the same form as Eq. (3) but with  $B_{\text{eff}}$  replacing  $B_v$ . However,  $B_{\text{eff}}$  is not directly related to  $\langle(1/r^2)_v\rangle$ , as in  $B_v$ , and this introduces some error in the RKR results. In the present case it is easy to estimate that the error introduced into the  $r_{\text{max}}$  and  $r_{\text{min}}$

TABLE III. Potential energy of the  $B^2\Pi$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	516.8	46 454	1.488	1.356	0.0641
1	1 540	47 477	1.545	1.315	0.191
2	2 549	48 486	1.588	1.289	0.316
3	3 545	49 482	1.625	1.269	0.440
4	4 519	50 456	1.658	1.253	0.560
5	5 492	51 429	1.690	1.239	0.681
6	6 447	52 384	1.719	1.226	0.799
7	7 390	53 327	1.748	1.215	0.917
8	8 323	54 260	1.776	1.205	1.032
9	9 238	55 175	1.804	1.196	1.146
10	10 144	56 081	1.831	1.188	1.258
11	11 030	56 967	1.857	1.180	1.368
12	11 911	57 848	1.883	1.173	1.477
13	12 772	58 709	1.909	1.167	1.584
14	13 609	59 546	1.935	1.161	1.688
15	14 463	60 400	1.962	1.154	1.793
16	15 293	61 230	1.989	1.147	1.896
17	16 081	62 018	2.015	1.142	1.994
18	16 859	62 796	2.041	1.136	2.091
19	17 612	63 549	2.068	1.130	2.184

<sup>a</sup> Experimental data from references 12-15.TABLE IV. Potential energy of the  $C^2\Pi$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	1 194	53 325	1.109	1.022	0.1481
1	3 556	55 687	1.148	0.997	0.4409
2	5 922	58 053	1.178	0.981	0.7343
3	8 192	60 323	1.204	0.970	1.016
4	10 491	62 622	1.228	0.961	1.301

<sup>a</sup> Experimental data from references 12-15.

is about 1%, and this error shows up in the fact that the calculated  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  curves cross at higher values of  $v$ . The potential energy curves, however, are still well within the accuracy required for most applications.

The curves for the various bound states of NO calculated by the RKR method are shown in Fig. 1 as the solid lines. The  $C^2\Pi$  and  $B^2\Pi$  curves are shown dashed over part of their range, because these curves cannot actually cross according to the noncrossing rule. The curves calculated here are the so-called "deperturbed" curves described in detail by Lagerqvist and Miescher.<sup>12</sup> The  $X^2\Pi_{1/2}$  and  $X^2\Pi_{3/2}$  states are represented by only one curve in Fig. 1, since the difference between them is too small to be shown on the scale used. This  $X^2\Pi$  curve is shown dashed at large distances, the dashed part being an extrapolation corresponding to a Hulburt-Hirschfelder<sup>7</sup> curve given by the equation

$$V(r) = 6.609[(1 - e^{-x})^2 + 0.06780x^3(1 + 2.663x)e^{-2x} - 1]\text{ev}, \quad (9)$$

where

$$x = 3.1579\left(\frac{r - r_e}{r_e}\right), \quad V(\infty) = 0,$$

and  $r_e = 1.1508$  Å is the position of the minimum. Equation (9) agrees with the RKR results within the error of the RKR method, and hence the extrapolation beyond the range of the RKR results can be made with some confidence. It might be mentioned in this connection that a Morse curve is in very poor agreement with the RKR results at large distances.

#### $^4\Pi$ STATE OF NO

Although the  $^4\Pi$  state of NO has been predicted by Mulliken<sup>4,5</sup> to be a bound state, it is considered sepa-

TABLE V. Potential energy for the  $D^2\Sigma^+$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	1157	54 239	1.109	1.020	0.1435
1	3437	56 519	1.147	0.993	0.4262
2	5671	58 753	1.176	0.975	0.7032
3	7854	60 936	1.202	0.961	0.9738
4	9973	63 055	1.225	0.950	1.237

<sup>a</sup> Experimental data from reference 13.

TABLE VI. Potential energy of the  $E^2\Sigma^+$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	1 183	61 811	1.112	1.025	0.1467
1	3 525	64 153	1.150	0.997	0.4371
2	5 835	66 463	1.177	0.980	0.7235
3	8 114	68 742	1.202	0.966	1.006
4	10 360	70 988	1.223	0.955	1.285
5	12 575	73 203	1.244	0.945	1.559

<sup>a</sup> Experimental data from references 16, 17.

rately because insufficient spectroscopic data are available for application of the RKR method. Ogawa<sup>20</sup> has found experimental evidence for a quartet-quartet transition in NO, which appears to be the same band system observed by Brook and Kaplan<sup>11</sup> and by Feast.<sup>16</sup> Ogawa has given plausible arguments for an assignment to a  $4\Sigma \rightarrow 4\Pi$  transition, with the  $4\Pi$  being the state predicted by Mulliken. The vibrational constants obtained by Ogawa for this state are  $\omega_e = 1019.0 \text{ cm}^{-1}$  and  $\omega_e x_e = 12.8 \text{ cm}^{-1}$ . To obtain a complete potential function for the  $4\Pi$  state, we use these vibrational constants and take advantage of the great similarity between the spectroscopic constants for corresponding states of the isoelectronic molecules NO and  $\text{O}_2^+$ . This similarity is illustrated in Table IX, where the spectroscopic constants are compared for the  $X^2\Pi$ ,  $4\Pi$ , and  $4\Sigma$  states. Thus a reasonable approximation for the  $4\Pi$  state of NO can be obtained by the use of the rotational constants for the  $a^4\Pi_u$  state of  $\text{O}_2^+$ .

The dissociation energy,  $D_e$ , of the  $4\Pi$  state of NO can be calculated to be 1.95 ev from the empirical relation

$$D_e = \frac{hc}{2} \left[ \frac{3\omega_e^2}{8\omega_e x_e - 3B_e} \right], \quad (10)$$

which Lippincott and Schroeder<sup>21</sup> have shown has an accuracy of about 5%. The use of a  $B_e$  value from  $\text{O}_2^+$  introduces a negligible error in the calculation. The Hulburt-Hirschfelder function for this state is therefore

$$V(r) = 1.95[(1 - e^{-x})^2 + 0.1741x^3(1 + 3.142x)e^{-2x} - 1] \text{ ev}, \quad (11)$$

TABLE VII. Potential energy of the  $A^2\Sigma^+$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	1 183	45 147	1.109	1.022	0.1467
1	3 525	47 489	1.147	0.995	0.4371
2	5 835	49 799	1.175	0.977	0.7235
3	8 111	52 075	1.199	0.964	1.006
4	10 354	54 318	1.220	0.953	1.284
5	12 564	56 528	1.242	0.943	1.558

<sup>a</sup> Experimental data from references 13, 16.<sup>20</sup> M. Ogawa, Science of Light (Tokyo) 3, 39 (1954).<sup>21</sup> E. R. Lippincott and R. Schroeder, J. Chem. Phys. 23, 1131 (1955).TABLE VIII. Potential energy of the  $B'^2\Delta$  state of NO.<sup>a</sup>

$v$	$V(\text{cm}^{-1})$	$T_e+V$ ( $\text{cm}^{-1}$ )	$r_{\text{max}}(\text{\AA})$	$r_{\text{min}}(\text{\AA})$	$V(\text{ev})$
0	604	60 968	1.368	1.246	0.07493
1	1789	62 153	1.424	1.209	0.2219
2	2943	63 307	1.466	1.186	0.3649
3	4062	64 426	1.503	1.168	0.5037
4	5177	65 541	1.539	1.153	0.6420
5	6212	66 576	1.570	1.139	0.7703

<sup>a</sup> Experimental data from reference 18.

where

$$x = 3.865 \left( \frac{r - r_e}{r_e} \right), \quad r_e = 1.38 \text{ \AA}, \quad V(\infty) = 0.$$

Equation (11) is based on the assumptions that the rotational constants for NO are almost identical with those for  $\text{O}_2^+$ , that the relation (10) holds, and that the Hulburt-Hirschfelder function is a good representation of the actual potential energy. On the basis of the information available, the first two assumptions seem quite reasonable, and the last assumption is made on the basis of the excellent agreement of the Hulburt-Hirschfelder function with the RKR calculations for the  $X^2\Pi$  state of NO. Equation (11) seems to be the best that can be given at present because of the scarcity of experimental information. It is shown in Fig. 1 as a dashed line.

#### RELATIONS AMONG THE STATES OF NO

A number of approximate but useful relations among the six different potential energy curves of NO can be obtained from simple quantum-mechanical theory.

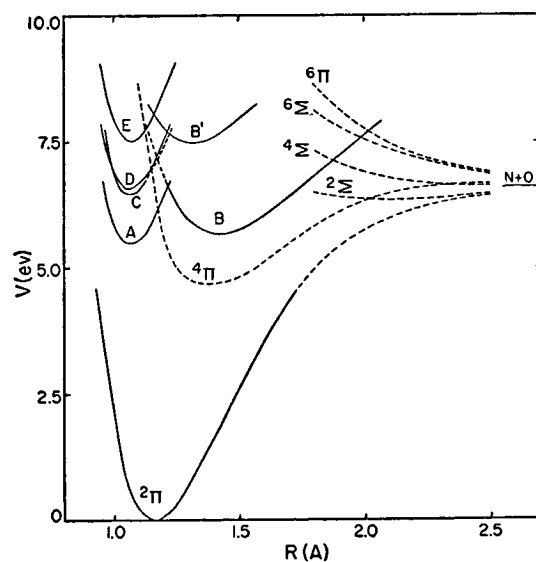


FIG. 1. Summary of N-O interactions. The solid lines were calculated by RKR method. The curves marked A, B, C, D, E, and B' correspond to the  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  states, respectively.

TABLE IX. Comparison of spectroscopic constants for corresponding states of the isoelectronic molecules NO and O<sub>2</sub><sup>+</sup>.<sup>a</sup>

State	$\omega_e(\text{cm}^{-1})$	$\omega_e x_e(\text{cm}^{-1})$	$B_e(\text{cm}^{-1})$	$\alpha_e(\text{cm}^{-1})$	$r_e(\text{\AA})$
X <sup>2</sup> Π					
O <sub>2</sub> <sup>+</sup>	1876.4	16.53	1.6722	0.01984	1.1227
NO	1904	13.97	1.7046	0.0178	1.1508
<sup>4</sup> Π					
O <sub>2</sub> <sup>+</sup>	1035.69	10.39	1.10466	0.01575	1.38126
NO	1019.0 <sup>b</sup>	12.8 <sup>b</sup>			
<sup>4</sup> Σ					
O <sub>2</sub> <sup>+</sup>	1196.77	17.09	1.28729	0.02206	1.27953
NO	1168.0 <sup>b</sup>	13.3 <sup>b</sup>			

<sup>a</sup> Unless otherwise stated, data are from reference 3, pp. 558, 560.<sup>b</sup> Reference 20.

These relationships can be used to calculate the long-range "tails" of the curves for the <sup>2</sup>Σ, <sup>4</sup>Σ, <sup>6</sup>Σ, and <sup>6</sup>Π states from those for the <sup>2</sup>Π and <sup>4</sup>Π states. The results are probably fairly reliable since theory is used only to obtain relations among energies, and not to calculate directly the energies themselves. Only the *p* electrons are considered. A similar procedure worked well in the case of N<sub>2</sub>, for which the usual perfect pairing approximation of simple valence-bond theory could be applied.<sup>2</sup> This approximation cannot be applied straightforwardly to NO because of the odd number of electrons, but can be used for all the electrons except those constituting the "three-electron bond."

The interaction energy according to the perfect pairing approximation can be written as follows<sup>22</sup>:

$$V = \sum J_{ij} - \frac{1}{2} \sum J_{ij} - \sum J_{ij} \quad (12)$$

orbitals with    orbitals with    orbitals with  
paired spins    nonpaired spins    parallel spins

where  $J_{ij}$  is the exchange integral for two electrons in the orbitals *i* and *j*. In Eq. (12) terms involving the Coulomb integrals have been omitted, since at large intermolecular separations the Coulombic interaction between neutral atoms is very small. According to the perfect pairing scheme, every electron should be paired, nonpaired, or antipaired with another electron, but this is impossible for NO with an odd number of electrons. However, Eq. (12) can be applied directly to four of the seven *p* electrons in NO, and with modification to the remaining three electrons.

An adequate description of the "three-electron bond" in NO can be given in terms of a combination of atomic and molecular orbitals, as suggested by Linnett.<sup>8</sup> For example, consider the  $\pi$  and  $\pi^*$  molecular orbitals of NO formed from the  $2p_y$  atomic orbitals of N and O. To a first approximation,

$$\begin{aligned} \pi 2p_y &= a 2p_{yN} + b 2p_{yO}, \\ \pi^* 2p_y &= a' 2p_{yN} - b' 2p_{yO}, \end{aligned} \quad (13)$$

where *a*, *b*, *a'*, and *b'* are all positive. Linnett now considers the case where one electron is on each MO, and the electrons have parallel spins. To the approximation that other electrons do not interfere, the wave function for these two electrons is

$$\begin{vmatrix} \pi(1)\alpha(1) & \pi^*(1)\alpha(1) \\ \pi(2)\alpha(2) & \pi^*(2)\alpha(2) \end{vmatrix}, \quad (14)$$

where  $\alpha$  is the usual electron spin function. By the rules of determinants Eq. (14) is equivalent within a numerical factor to

$$\begin{vmatrix} 2p_{yN}(1)\alpha(1) & 2p_{yO}(1)\alpha(1) \\ 2p_{yN}(2)\alpha(2) & 2p_{yO}(2)\alpha(2) \end{vmatrix}. \quad (15)$$

Thus to describe these two electrons it is immaterial whether they are said to occupy the  $\pi 2p_y$  and  $\pi^* 2p_y$  molecular orbitals or the  $2p_{yN}$  and  $2p_{yO}$  atomic orbitals. If now a third electron having  $\beta$  spin is added to the  $\pi 2p_y$  orbital, the situation can still be described as the two electrons with  $\alpha$  spin occupying atomic orbitals and the one electron with  $\beta$  spin occupying a molecular orbital. According to the perfect pairing scheme, the pair of electrons in the AO's contribute an energy of  $-J_{yy}$  to the total interaction. The electron in the MO forms a one-electron bond, and the strength of such a bond is usually about one-half that of the corresponding two-electron bond.<sup>23</sup> Thus the contribution of the single electron is  $+\lambda J_{yy}$ , where  $\lambda \approx \frac{1}{2}$ , and the energy of the "three-electron bond" is  $-(1-\lambda)J_{yy}$ .

It should be mentioned that this formulation of the energy of a three-electron bond neglects resonance and so leads to a net antibonding of about  $-\frac{1}{2}J$ . If the two nuclei are very similar, so that  $a \approx b$  in Eq. (13), there will be an additional bonding due to resonance,<sup>24</sup> and the energy will be<sup>25</sup> approximately  $-(1-\lambda)J + \mu J$ . For the case of exact resonance ( $a=b$ ), such as in He<sub>2</sub><sup>+</sup>,  $\mu=1$  and the three-electron bond then contributes a net bonding of about  $+\frac{1}{2}J$ , as expected,<sup>24</sup> but for weak resonance,  $\mu \approx 0$  and the net effect is antibonding. For NO at large internuclear separations we have taken  $\mu$  to be zero, since the energies of the relevant resonance structures,<sup>24</sup>  $\cdot\text{N}=\text{O}$ : and  $\text{:}\ddot{\text{N}}=\text{O}\cdot^+$ , are quite different at large separations, as shown by the difference in the ionization potential of O(13.6 eV)<sup>26</sup> and the electron affinity of N ( $\sim 0$  eV).<sup>27</sup> At smaller separations there may be some resonance stabilization, but the large change in binding energy when the odd

<sup>22</sup> Reference 22, p. 151.<sup>23</sup> L. Pauling, *Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1945), second edition, pp. 264-267.<sup>24</sup> Reference 22, pp. 231-233.<sup>25</sup> G. Herzberg, *Atomic Spectra and Atomic Structure* (Dover Publications, New York, 1944), p. 200.<sup>26</sup> H. S. W. Massey, *Negative Ions* (Cambridge University Press, London, 1950), pp. 18-19.<sup>27</sup> C. A. Coulson, *Valence* (Oxford University Press, London, 1952), pp. 166-184.

TABLE X. States of NO dissociating into ground-state atoms. The electrons in brackets constitute "three-electron bonds"; the other electrons can be handled by the perfect pairing approximation.

State	MO description	AO+MO description (Linnett)*	Interaction energy by modified perfect pairing approximation
${}^6\Pi$	$(\sigma 2p_x)(\sigma^* 2p_x)(\pi 2p_y)(\pi^* 2p_y)[(\pi 2p_z)^2(\pi^* 2p_z)]$	$(2p_{xN}, 2p_{xO})(2p_{yN}, 2p_{yO})[(2p_{zN}, 2p_{zO})(\langle \pi 2p_z \rangle)]$	$-J_{xx} - (2-\lambda)J_{yy}$
${}^6\Sigma$	$(\pi 2p_y)(\pi^* 2p_y)(\pi 2p_z)(\pi^* 2p_z)[(\sigma 2p_x)^2(\sigma^* 2p_x)]$	$(2p_{yN}, 2p_{yO})(2p_{zN}, 2p_{zO})[(2p_{xN}, 2p_{xO})(\langle \sigma 2p_x \rangle)]$	$-(1-\lambda)J_{xx} - 2J_{yy}$
${}^4\Sigma$	$(\pi 2p_y)^2(\pi 2p_z)(\pi^* 2p_z)[(\sigma 2p_x)^2(\sigma^* 2p_x)]$	$(\pi 2p_y)^2(2p_{zN}, 2p_{zO})[(2p_{xN}, 2p_{xO})(\langle \sigma 2p_x \rangle)]$	$-(1-\lambda)J_{xx}$
${}^2\Sigma$	$(\pi 2p_y)^2(\pi 2p_z)^2[(\sigma 2p_x)^2(\sigma^* 2p_x)]$	$(\pi 2p_y)^2(\pi 2p_z)^2[(2p_{xN}, 2p_{xO})(\langle \sigma 2p_x \rangle)]$	$-(1-\lambda)J_{xx} + 2J_{yy}$
${}^4\Pi$	$(\sigma 2p_x)^2(\pi 2p_y)(\pi^* 2p_y)[(\pi 2p_z)^2(\pi^* 2p_z)]$	$(\sigma 2p_x)^2(2p_{yN}, 2p_{yO})[(2p_{zN}, 2p_{zO})(\langle \pi 2p_z \rangle)]$	$J_{xx} - (2-\lambda)J_{yy}$
${}^2\Pi$	$(\sigma 2p_x)^2(\pi 2p_y)^2[(\pi 2p_z)^2(\pi^* 2p_z)]$	$(\sigma 2p_x)^2(\pi 2p_y)^2[(2p_{zN}, 2p_{zO})(\langle \pi 2p_z \rangle)]$	$J_{xx} + \lambda J_{yy}$

\*  $\langle \rangle$  around a singly occupied orbital signify that the electron has  $\beta$  spin. Absence of  $\langle \rangle$  signifies  $\alpha$  spin.

electron is removed ( $D_0(\text{NO}^+) - D_0(\text{NO}) = 4.1 \text{ eV}$ )<sup>28</sup> indicates that such stabilization is probably slight.

Application of these ideas to various states of NO is shown in Table X. The first column gives the term symbol for the state and the second column gives the conventional simple MO description. The third column gives the description according to the Linnett procedure. In both of these columns only the group of three electrons set off by brackets needs special consideration, and the other four electrons can be treated straightforwardly by the perfect pairing approximation. In the fourth column of Table X are given the expressions for the interaction energies according to the modified perfect pairing scheme, in which the three electrons in the brackets are treated according to the foregoing discussion as contributing an energy of the form  $-(1-\lambda)J$ . The  $x$  axis is chosen to lie along the internuclear axis, and by symmetry  $J_{xx} \neq J_{yy} = J_{zz}$ , and  $J_{xy} = J_{yz} = J_{zx} = 0$ . The following relations among the interaction energies are easily derived from Table X:

$$V({}^2\Sigma) = \frac{1}{2}\lambda(3-\lambda)V({}^2\Pi) - \frac{1}{2}(1+\lambda)(2-\lambda)V({}^4\Pi), \quad (16)$$

$$V({}^4\Sigma) = -\frac{1}{2}(1-\lambda)(2-\lambda)V({}^2\Pi) - \frac{1}{2}\lambda(1-\lambda)V({}^4\Pi), \quad (17)$$

$$V({}^6\Sigma) = -[2 - \frac{1}{2}\lambda(3-\lambda)]V({}^2\Pi) + [1 - \frac{1}{2}\lambda(1-\lambda)]V({}^4\Pi), \quad (18)$$

$$V({}^6\Pi) = -(2-\lambda)V({}^2\Pi) + (1-\lambda)V({}^4\Pi). \quad (19)$$

These relations, together with  $\lambda \approx \frac{1}{2}$  and the previously obtained curves for the  ${}^2\Pi$  and  ${}^4\Pi$  states, give the curves for the  ${}^2\Sigma$ ,  ${}^4\Sigma$ ,  ${}^6\Sigma$ , and  ${}^6\Pi$  states, which are shown as dashed lines in Fig. 1.

It is difficult to assess the absolute accuracy of the potential energies calculated by the foregoing modified perfect pairing approximation, since there is no definite experimental information on the  ${}^2\Sigma$ ,  ${}^4\Sigma$ ,  ${}^6\Sigma$ , and  ${}^6\Pi$  states. Gaydon<sup>29</sup> and others have suggested that the

${}^2\Sigma$  state predissociates the  $B {}^2\Pi$  state and is responsible for the lack of any observed emission in the  $\beta$ -band system ( $B {}^2\Pi \rightarrow X {}^2\Pi$ ) for  $v > 7$ . The present calculations are consistent with this suggestion, since the  ${}^2\Sigma$  curve is predicted to cross the  $B {}^2\Pi$  curve somewhere between  $v=6$  and  $v=7$ . In the absence of definite checks, however, it is well to calculate the potential energies by another method. It can be shown that they are at least consistent with the previously calculated energies for the  $\text{N}_2$  states. Since oxygen follows nitrogen in the periodic table, it seems reasonable to suppose that the  ${}^2\Pi$  ground state of NO can be approximately described as the  ${}^1\Sigma$  ground state of  $\text{N}_2$  with one electron added. The interaction energy for the  $X {}^1\Sigma$  state of  $\text{N}_2$  has been given as<sup>2</sup>

$$V({}^1\Sigma\text{N}_2) = J_{xx} + 2J_{yy} = -317.8e^{-2.753r} \text{ eV}, \quad 1.3 \text{ \AA} < r < 3.2 \text{ \AA}, \quad (20)$$

and that for the  $X {}^2\Pi$  state of NO is

$$V({}^2\Pi\text{NO}) = J_{xx} + \lambda J_{yy}, \quad (21)$$

which is given numerically by Eq. (9). With  $\lambda \approx \frac{1}{2}$ , the values of  $J_{xx}$  and  $J_{yy}$  can be calculated as a function of distance from Eqs. (20) and (21), and these values substituted into the relations given in Table X to obtain the interaction energies for the  ${}^4\Pi$ ,  ${}^2\Sigma$ ,  ${}^4\Sigma$ ,  ${}^6\Sigma$ , and  ${}^6\Pi$  states of NO at large separations ( $r > 1.8 \text{ \AA}$ ). The curves calculated in this way agree remarkably well with those shown in Fig. 1, with a difference that is too small to be shown on the scale of the figure. The agreement is within 10% unless the interaction energy is small so that the percentage deviation increases. The surprising thing is that both calculation methods predict a slight hump of about 0.04 eV in the  ${}^4\Pi$  curve at about  $r = 2.4 \text{ \AA}$ . We do not attach much significance to this hump because of the approximations made, however.

The potential energies of the  ${}^2\Sigma$ ,  ${}^4\Sigma$ ,  ${}^6\Sigma$ , and  ${}^6\Pi$  states of NO can be represented with sufficient accuracy in the

<sup>28</sup> Reference 3, p. 558.

<sup>29</sup> A. G. Gaydon, J. Chem. Phys. 16, 607 (1948).



range  $1.8 \text{ \AA} < r < 2.8 \text{ \AA}$  by the following expressions:

$$V(^2\Sigma) = 0.26[e^{-3.8(r-2.0)} - 2e^{-1.9(r-2.0)}] \text{ ev}, \quad (22)$$

$$V(^4\Sigma) = 430e^{-3.570r} \text{ ev}, \quad (23)$$

$$V(^6\Sigma) = 138e^{-2.492r} \text{ ev}, \quad (24)$$

$$V(^6\Pi) = 351e^{-2.866r} \text{ ev}, \quad (25)$$

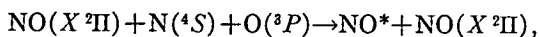
relative to an energy zero corresponding to infinitely separated ground-state N and O atoms. The expressions for the  $^2\Pi$  and  $^4\Pi$  states have been given by Eqs. (9) and (11), respectively.

### DISCUSSION OF NO STATES

Although there is no direct experimental information on the  $^2\Sigma$ ,  $^4\Sigma$ ,  $^6\Sigma$ , and  $^6\Pi$  states, some indirect spectroscopic evidence pertaining to some of these states exists. It is therefore important to show that the calculated curves for these states are at least consistent with the spectroscopic observations. It has already been mentioned that Gaydon has suggested that the  $^2\Sigma$  state is responsible for the absence of the emission bands for the higher vibrational levels of the  $B^2\Pi$  state. Actually, the complete lack of emission bands suggests that the cause is predissociation by a  $\Pi$  state rather than a  $\Sigma$  state, because both  $\Lambda$ -doublet components are missing.<sup>30</sup> If this is the case, the only possibility is the  $^4\Pi$  state, which would cross the  $B^2\Pi$ – $C^2\Pi$  curve at the proper energy level at about  $r = 1.15 \text{ \AA}$  (see Fig. 1). Even though the selection rule  $\Delta S = 0$  is not fulfilled for this predissociation, a breaking-off in emission bands with no broadening of absorption bands may still occur.<sup>31</sup>

The  $^4\Pi$  state may also be responsible for the predissociation observed in the  $\delta$  bands ( $C^2\Pi \rightarrow X^2\Pi$ ) during photodecomposition,<sup>32</sup> which occurs at about the  $v = 1$  vibrational level of the  $C^2\Pi$  state. Such a predissociation could be caused by the crossing at  $1.15 \text{ \AA}$ .

Tanaka,<sup>33</sup> repeating the work of Gaydon,<sup>34</sup> found that no bands were observed in the afterglow spectrum of NO which corresponded to energies much higher than the dissociation energy of the ground state of NO. The highest observed vibrational levels were  $v = 6$  for the  $B^2\Pi$  state,  $v = 0$  for the  $C^2\Pi$ , and  $v = 3$  for the  $A^2\Sigma^+$ . Tanaka proposed the three-body reaction,



to account for these facts. However, according to our results, a possible explanation is curve crossing by

either the  $^2\Sigma$  or  $^4\Pi$  states.<sup>†</sup> These curve crossings might also help serve to explain abnormal intensity distributions in some bands of the afterglow spectrum.<sup>33</sup>

It is thus seen that the present results appear to be consistent with spectroscopic observations.

### O–N<sub>2</sub> AND O<sub>2</sub>–N<sub>2</sub> INTERACTIONS

The modified perfect pairing scheme of the preceding sections makes it possible to calculate approximate long-range potential energies for the O–N<sub>2</sub> and O<sub>2</sub>–N<sub>2</sub> interactions, since a pairing scheme automatically describes these interactions as just the sums of the interactions between the individual atoms of the different molecules. Consider the interaction of a nitrogen atom,  $\text{N}(2p_x)(2p_y)(2p_z)$ , with an oxygen atom,  $\text{O}(2p_x)(2p_y)(2p_z)^2$ . If either or both of these atoms are bound into some other molecule, the spins of the electrons must be uncorrelated or nonpaired. By Eq. (12) the  $p_x$  and  $p_y$  electrons will contribute a net repulsion of  $-\frac{1}{2}(J_{xx} + J_{yy})$  to the interaction energy, and the  $p_z$  electrons will contribute a net repulsion of  $-\frac{1}{2}(J_{zz} + J_{zz})$ , so that the total interaction energy is

$$V(\text{O} \cdots \text{N}) = -\frac{1}{2}J_{xx} - \frac{1}{2}J_{yy} - J_{zz} = -\frac{1}{2}J_{xx} - \frac{3}{2}J_{yy}. \quad (26)$$

The same results follows if the roles of the  $p_y$  and  $p_z$  electrons are interchanged. The configuration  $\text{O}(2p_x)^2(2p_y)(2p_z)$  gives rise to a considerably higher interaction energy, and is therefore not considered. From Table X it is easy to calculate  $V(\text{O} \cdots \text{N})$  in terms of the interaction energies for the NO states with  $\lambda \approx \frac{1}{2}$ , for example,

$$V(\text{O} \cdots \text{N}) \approx V(^6\Pi) - V(^4\Sigma), \quad (27)$$

which can be represented by

$$V(\text{O} \cdots \text{N}) = 161e^{-2.654r} \text{ ev}, \quad 1.8 \text{ \AA} < r < 2.8 \text{ \AA}. \quad (28)$$

The O–N<sub>2</sub> and O<sub>2</sub>–N<sub>2</sub> interactions are obtained by simply adding up all pertinent  $\text{O} \cdots \text{N}$  interactions, each one of which would be given by Eq. (28) with the value of  $r$  appropriate for the atom-atom distance. The dependence of the O–N<sub>2</sub> and O<sub>2</sub>–N<sub>2</sub> interactions on orientation is thus given implicitly by the dependence of the atom-atom distances on the molecular orientations.

In many cases it is useful to have the total interaction energy averaged over all orientations. The method of averaging has already been worked out in connection with the various nitrogen interactions,<sup>2</sup> and the same method is applicable here. The average energy of interaction for an oxygen atom at a distance  $R$  from

<sup>†</sup> Barth, Schade, and Kaplan [J. Chem. Phys. **30**, 347 (1959)] have recently found changes in the intensity distribution of the NO afterglow emission spectrum upon addition of rare gas. They argue that this is strong experimental evidence that the afterglow spectrum arises from the three-body recombination of a ground-state oxygen atom and a ground-state nitrogen atom by way of some intermediate state into the excited upper states.

<sup>30</sup> Reference 3, p. 418.

<sup>31</sup> Reference 3, p. 419.

<sup>32</sup> P. J. Flory and H. L. Johnston, J. Am. Chem. Soc. **57**, 2641 (1935); J. Chem. Phys. **14**, 212 (1946).

<sup>33</sup> Y. Tanaka, J. Chem. Phys. **22**, 2045 (1954).

<sup>34</sup> A. G. Gaydon, Proc. Phys. Soc. (London) **A56**, 160 (1944).

the center of mass of a nitrogen molecule is

$$\langle V(R) \rangle = 2V_0 e^{-aR} (a^2 R d)^{-1} [2(aR+1) \sinh(ad/2) - 2(ad/2) \cosh(ad/2)], \quad (29)$$

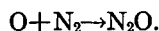
where  $V_0$  and  $a$  are the parameters of Eq. (28) and  $d$  is the bond length of the molecule. The range of validity of Eq. (29) evidently depends on the range of validity of Eq. (28). The limits of the range are given by<sup>2</sup>

$$\langle R \rangle = r[1 + \frac{1}{2}(d/r)^2]. \quad (30)$$

The average potential for the O—N<sub>2</sub> interaction calculated in this manner can be represented by

$$\langle V(R) \rangle = 357 e^{-2.603R} \text{ ev}, \quad R \text{ in A.} \quad (31)$$

According to Eq. (30), this potential is valid from 1.9 A to 2.8 A. However, at close distances of approach and certain favorable orientations, a strong attraction can set in which leads to the reaction,



Since this reaction has a heat of activation of only 12 to 14 kcal<sup>35</sup> (0.5 to 0.6 ev), we must restrict the lower limit of Eq. (31) to about 2.5 A. Since most collisions will not lead to reaction because of unfavorable orientation, we expect Eq. (31) to be fairly reliable in the range from 2.5 A to 2.8 A. It is interesting to note that the O—N<sub>2</sub> interaction is important in the calculation of the transport properties of air only between 1800° and 6000°K.<sup>1</sup> According to Hirschfelder and Eliason,<sup>36</sup> the important part of the potential curve for such calculations is around  $V(r) = \theta kT$ , where  $k$  is Boltzmann's constant and  $\theta$  is approximately unity. Hence it is desirable to know the O—N<sub>2</sub> potential from about 0.16 to 0.52 ev. Eq. (31) covers most of this range, varying from 0.24 to 0.54 ev.

The average O<sub>2</sub>—N<sub>2</sub> potential is similarly found to be

$$\begin{aligned} \langle V(R) \rangle = & 4V_0 e^{-aR} (a^3 R d_1 d_2)^{-1} \\ & \times [4(aR+2) \sinh(ad_1/2) \sinh(ad_2/2) \\ & - 4(ad_1/2) \sinh(ad_2/2) \cosh(ad_1/2) \\ & - 4(ad_2/2) \sinh(ad_1/2) \cosh(ad_2/2)], \quad (32) \end{aligned}$$

where  $R$  is the distance between the centers of mass of the molecules, and  $d_1$  and  $d_2$  are the bond lengths of the molecules. The range of validity is

$$\langle R \rangle = r[1 + \frac{1}{2}(d_1/r)^2 + \frac{1}{2}(d_2/r)^2]. \quad (33)$$

Substitution of Eq. (28) into Eqs. (32) and (33) gives results which can be represented by the equation

$$\langle V(R) \rangle = 762 e^{-2.524R} \text{ ev}, \quad 1.9 \text{ A} < R < 2.9 \text{ A}. \quad (34)$$

<sup>35</sup> Quoted from P. Hartek and S. Dondes, *J. Chem. Phys.* **26**, 1727 (1957).

<sup>36</sup> J. O. Hirschfelder and M. A. Eliason, *Ann. N. Y. Acad. Sci.* **67**, 451 (1957).

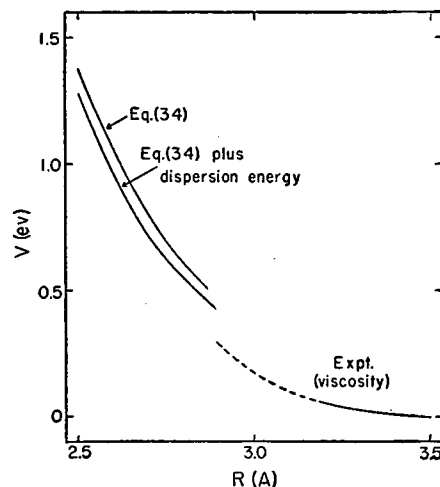


Fig. 2. Average O<sub>2</sub>—N<sub>2</sub> interaction energy as obtained by different methods: (a) modified perfect pairing scheme, Eq. (34); (b) Eq. (34) plus dispersion energy; (c) semiempirical results from viscosities of O<sub>2</sub> and N<sub>2</sub>.

Equation (34) can be compared with a similar potential derived from measurements of the viscosities of N<sub>2</sub> and O<sub>2</sub> at high temperatures, as explained below, and the comparison is shown in Fig. 2. Since Eq. (34) is the result of essentially only a first-order perturbation calculation, it is interesting to add on the second-order perturbation energy, the London dispersion energy, which is given approximately by the expression<sup>37</sup>

$$\langle V(\text{dis}) \rangle = -\frac{3}{2} \frac{\bar{\alpha}_1 \bar{\alpha}_2}{R^6} \left( \frac{I_1 I_2}{I_1 + I_2} \right) = -\frac{29.2}{R^6} \text{ ev}, \quad R \text{ in A}, \quad (35)$$

where  $\bar{\alpha}_1$  and  $\bar{\alpha}_2$  are the average polarizabilities of the molecules and  $I_1$  and  $I_2$  are their ionization potentials. The sum of Eqs. (34) and (35) is also shown in Fig. 2. Although the results do not overlap, they appear to be consistent, and the gap between 2.9 A and 3.2 A could be covered by a reasonable interpolation.<sup>§</sup>

The interactions derived from high temperature viscosities are based on an exp-six potential energy function, which can be written in the form

$$\langle V(R) \rangle = \frac{\epsilon}{1 - 6/\alpha} \left[ \frac{6}{\alpha} e^{\alpha(1 - R/R_m)} - \left( \frac{R_m}{R} \right)^6 \right], \quad (36)$$

where  $\epsilon$  is the depth of the small van der Waals minimum in the potential energy,  $R_m$  is the position of the minimum, and  $\alpha$  is a dimensionless parameter which is a measure of the steepness of the repulsion energy. This form of function is used in preference to the Lennard-Jones (12-6) potential, which represents the

<sup>37</sup> Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 963.

<sup>§</sup> The referee has kindly pointed out that the consistency would appear somewhat better if higher terms, varying as  $R^{-8}$ ,  $R^{-10}$ , etc., were included in Eq. (35). We feel, however, that the over-all accuracy of Eq. (34) is probably not great enough to justify such a refinement.

repulsion by an inverse twelfth power instead of an exponential, in the expectation that the exponential is physically more realistic. The parameters of Eq. (36) have previously been determined from viscosity data for  $N_2$ , and found to be<sup>38</sup>:  $\alpha=17.0$ ,  $R_m=4.011$  Å,  $\epsilon/k=101.2^\circ\text{K}$ . Exactly the same procedure can be applied to  $O_2$ , and the parameters are found to be:  $\alpha=17.0$ ,  $R_m=3.726$  Å,  $\epsilon/k=132^\circ\text{K}$ . The viscosity measurements used included the recent results of Raw and Ellis<sup>39</sup> at high temperatures, as well as previous results of other investigators<sup>40</sup> at lower temperatures. Parameters for the  $N_2-O_2$  interaction can then be calculated from those for  $N_2-N_2$  and  $O_2-O_2$  by means of semiempirical combination rules,<sup>41</sup> to yield

$$N_2-O_2: \alpha=17.0, \quad R_m=3.861 \text{ Å}, \quad \epsilon/k=116^\circ\text{K}.$$

These values, when substituted into Eq. (36), yield the curve for viscosity shown in Fig. 2. It is estimated from the temperature range of the viscosity measurements that this curve is not valid for distances smaller than about 3.2 Å.

### SUMMARY

Potential energy curves for the interactions between a ground-state N atom and a ground-state O atom have been calculated from spectroscopic data and from approximate quantum-mechanical relations. The interaction corresponding to the  $X^2\Pi$  state of NO was calculated from spectroscopic data by the RKR method, with the results as given in Tables I and II. This interaction is well represented by the Hulburt-Hirschfelder function given in Eq. (9). A Hulburt-Hirschfelder function has also been given in Eq. (11) for the  $^4\Pi$  state. This result is based on a limited amount of spectroscopic information and on the close analogy of NO with  $O_2^+$ . Relations among the six states of NO dissociating to ground state atoms have been obtained by a modified perfect pairing scheme, based on a description of electronic configuration in terms of a

combination of atomic and molecular orbitals suggested by Linnett. On the basis of these relations, the curves for the  $^2\Sigma$ ,  $^4\Sigma$ ,  $^6\Sigma$ , and  $^6\Pi$  states have been calculated from those for the  $^2\Pi$  and  $^4\Pi$  states. A partial check on these results has been made by calculating the  $^4\Pi$ ,  $^2\Sigma$ ,  $^4\Sigma$ ,  $^6\Sigma$ , and  $^6\Pi$  curves from the known curves for the  $X^1\Sigma_g^+$  state of  $N_2$  and the  $X^2\Pi$  state of NO. The agreement is very good. The potential energies for the  $^2\Sigma$ ,  $^4\Sigma$ ,  $^6\Sigma$ , and  $^6\Pi$  states have been represented empirically by Eqs. (22)–(25).

Sections of curves corresponding to interactions involving excited atoms (the  $A^2\Sigma^+$ ,  $B^2\Pi$ ,  $C^2\Pi$ ,  $D^2\Sigma^+$ ,  $E^2\Sigma^+$ , and  $B'^2\Delta$  states of NO) have also been calculated by the RKR method, and are given in Tables III–VIII.

A brief discussion has been given which indicates that the calculated NO curves are consistent with indirect spectroscopic evidence. The suggestion has been made that the  $^4\Pi$  state may play an important role in the afterglow problem.

The modified perfect pairing scheme has also been used to derive relations which permit the  $O-N_2$  and  $O_2-N_2$  interactions to be determined in terms of the previously derived N–O interactions. The  $O-N_2$  and  $O_2-N_2$  interactions can be obtained as implicit functions of orientation from Eq. (28), and the interactions averaged over all orientations are given by Eqs. (31), (34), and (35). The average  $O_2-N_2$  interaction is consistent with a semiempirical average interaction derived from high-temperature gas viscosity data.

It is difficult to assess the absolute accuracy of the results because of the limited experimental data. The results are at least consistent with one another and with available data. Furthermore, they are based on methods similar to those previously used to obtain interactions for nitrogen, for which a larger number of checks with experiment were possible. It is believed that the present results are the best that can be obtained on the basis of present experimental information.

### ACKNOWLEDGMENTS

The authors wish to thank Dr. E. R. Lippincott for several interesting discussions and for his help in locating spectroscopic data, and Mr. L. T. Ho for his help with some of the calculations.

<sup>38</sup> E. A. Mason and W. E. Rice, J. Chem. Phys. **22**, 843 (1954).

<sup>39</sup> C. J. G. Raw and C. P. Ellis, J. Chem. Phys. **28**, 1198 (1958).

<sup>40</sup> M. Trautz and A. Melster, Ann. Physik **7**, 409 (1930); M. Trautz and R. Zink, *ibid.* **7**, 427 (1930); M. Trautz and R. Heberling, *ibid.* **10**, 155 (1931); H. L. Johnston and K. E. McCloskey, J. Phys. Chem. **44**, 1038 (1940); R. Wobser and F. Müller, Kolloid-Beih. **52**, 165 (1941).

<sup>41</sup> E. A. Mason, J. Chem. Phys. **23**, 49 (1955).